

# PATENT SPECIFICATION

(11) 1439 000

1439 000

- (21) Application No. 55063/73 (22) Filed 28 Nov. 1973  
 (31) Convention Application No. 2258301 (32) Filed 29 Nov. 1972 in  
 (33) Germany (DT)  
 (44) Complete Specification published 9 June 1976  
 (51) INT CL<sup>3</sup> C11D 3/36  
 (52) Index at acceptance



C5D 6A5B 6A5C 6A5E 6A8B 6A9 6B10A 6B12B1 6B12E  
 6B12F1 6B12G1 6B12G2A 6B12G4 6B12N1 6B15  
 6B1 6B2 6B3 6B7 6B8 6C6 6C8

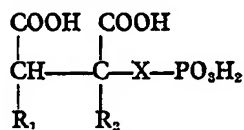
## (54) WASHING COMPOSITIONS AND WASHING ASSISTANTS FOR TEXTILES

(71) We, HENKEL & CIE. GMBH., a German Company, of 67 Henkelstrasse, Duesseldorf-Holthausen 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The action of the known washing compositions and washing assistants depends to a substantial extent on the presence of complex-forming compounds for alkaline earth ions. These complex-forming compounds assist the action of other, non-complex-forming inorganic or organic washing composition components. Such complex-forming compounds include, for example, sodium tripolyphosphate. In publications in connection with questions of protection of the environment the use of these complex-forming compounds in washing compositions and washing assistants has been criticised; in this connection the view is often taken that the nutritional properties of the water courses etc. may be largely due to the phosphorus compounds which arrive in the waterways by such means. Therefore the requirement for washing compositions and washing assistants with a lower content of phosphorus has been put forward.

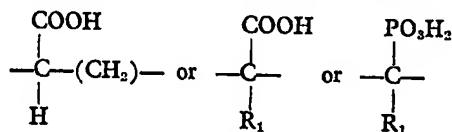
The object of the invention is to replace the known phosphorus-containing complex-forming compounds in washing compositions and washing assistants for textiles by complex-forming compounds which have only a small content of phosphorus, but which in their complex-forming action are not inferior to an equal amount by weight of sodium tripolyphosphate.

According to the present invention, therefore, a builder component poor in phosphorus is used which contains as the phosphorus substitute a phosphonopolycarboxylic acid of the formula I



(I)

or a water-soluble salt thereof, in which  $\text{R}_1$  represents a hydrogen atom or the methyl residue,  $\text{R}_2$  represents a hydrogen atom, an alkyl residue having 1 to 4 carbon atoms or the residue  $-\text{CH}_2-\text{CHR}_1-\text{COOH}$  wherein  $\text{R}_1$  has the above meaning, and X represents a direct bond or the group



wherein  $\text{R}_1$  has the above meaning and in which a maximum of three carboxyl groups may preferably be present.

By phosphonopolycarboxylic acids of formula I and their water-soluble salts, subsequently denoted as "phosphono - polycarboxylic acids" or "PPC", are meant the free acids and such compounds in which the hydrogen of the phosphonic acid group and the carboxyl groups are wholly or partly replaced by an alkali metal, especially sodium, or by ammonium. The water-soluble salts with organic bases, especially aliphatic amines and alkylolamines having not more than 6 carbon atoms in the molecule are also suitable.

The PPC may represent the builder substance alone, but it may also be used in combination with alkaline reacting salts which have no, or not sufficient, complex-forming power for alkaline earth ions, so as to prevent the precipitation of alkaline earth salts.

The washing compositions and washing assistants according to the invention contain:—

(I) 0.5—70% by weight of a phosphonopolycarboxylic acid of the above defined formula I,

(II) 0—96.5% by weight of a complex-forming and/or non-complex-forming, preferably phosphorus-free, builder substance, other than (I) above,

(III) 3—45% by weight of at least one surface-active compound from the group of

soaps, synthetic carboxylates, sulphates, sulphates and non-ionic polyglycolethers,

- 5 while the components of the washing compositions and washing assistants, especially phosphonopolycarboxylic acid and the other builder substances, are chosen so that the preparations in 1% aqueous solution have a pH value between 6 and 11.5, preferably between 7 and 11.

- 10 The preparations according to the invention may contain in addition other conventional washing composition components, as for example a bleaching component, textile softeners, brighteners, dirt carriers, foam regulators, enzymes, dyestuffs and perfumes, and water.

The following phosphonopolycarboxylic acids, for example, are suitable according to the invention:

- 20 1 - Phosphonoethane - 1,2 - dicarboxylic acid, 2 - phosphonopropane - 2,3 - dicarboxylic acid, 1 - phosphonopropane - 1,2,3 - tricarboxylic acid, 1 - phosphonopropane - 1,2 - dicarboxylic acid, 1 - phosphono - 2 - methylpropane - 1,2,3 - tricarboxylic acid, 25 2 - phosphonobutane - 2,3 - dicarboxylic acid, 2 - phosphonobutane - 2,3,4 - tricarboxylic acid, 2 - phosphonobutane - 1,2,4 - tricarboxylic acid, 1 - phosphonobutane - 1,2,3 - tricarboxylic acid, 1 - phosphono - 2 - methylbutane - 1,2,3 - tricarboxylic acid, 2 - phosphono - 3 - methylbutane - 2,3,4 - tricarboxylic acid, 2 - phosphonopentane - 2,3,4 - tricarboxylic acid, 2 - phosphono - 3 - methylpentane - 2,3,4 - tricarboxylic acid, 1,1 - diphosphonopropane - 2,3 - dicarboxylic acid, 1,1 - diphosphono - 2 - methylpropane - 2,3 - dicarboxylic acid, 2,2 - diphosphonobutane - 3,4 - dicarboxylic acid, 1,1 - diphosphonobutane - 2,3 - dicarboxylic acid, 2,2 - diphosphono - 3 - methylbutane - 3,4 - dicarboxylic acid, 2,2 - diphosphonopentane - 3,4 - dicarboxylic acid, 1,1 - diphosphono - 2 - methylbutane - 2,3 - dicarboxylic acid, 45 2,2 - diphosphono - 3 - methylpentane - 3,4 - dicarboxylic acid.

- The phosphorus content of the phosphonopolycarboxylic acids to be used according to the invention, referred to the sodium salts, is mostly less than half of the phosphorus content of an equal amount by weight of sodium tripolyphosphate. In the compositions according to the invention the height of the total phosphorus content thereof depends on whether the phosphorus-poor builder component of these compositions consists only of PPC or of a combination of PPC with other builder substances, preferably alkali metal carbonates and/or alkali metal silicates. The phosphorus content of the compositions according to the invention does not lie above 4% by weight, preferably not over 2% by weight; it therefore amounts to less than

2/5, usually less than 1/5 of the total phosphorus content of a comparable composition based on tripolyphosphate. 65

The phosphorus-poor builder component of the compositions according to the invention preferably contains PPC together with an alkali metal carbonate and/or an alkali metal silicate, while the proportion by weight of PPC to the carbonate and/or silicate lies between 1:100 and 4:1, preferably 1:50 and 4:1, and especially between 1:20 and 1:1. 70

The composition of the washing compositions and washing assistants of the invention depends largely on their purpose of use. Products according to the invention, which are softeners and compositions which are to be used as pre-washing agents, generally have a pH value between 9.5 and 11 in 1% aqueous solution, like the said boiling or universal or complete washing composition, which pH value is usually obtained by a larger content of basically reacting substances. Products which are used as fine washing and coloured washing agents, are usually neutral (pH 7) to weakly alkaline (pH 9.5) in 1% aqueous solution, but are also sometimes weakly acid (pH 6—7). The boiling or universal or complete washing compositions also differ from the other preparations by containing a bleaching component, consisting of peroxy-compounds, stabilisers and in some cases activators for the peroxy compounds. The bleaching component may constitute 10—50% by weight, preferably 15—40% by weight of the total washing composition. 85

The foam-inhibited washing compositions, preferably intended for use in washing machines, are of special importance in practice, in which the surface-active component has the following composition: 90

8—95, preferably 25—75% by weight of one or more surface-active compounds of the sulphonate and/or sulphate type, 105

0—80, preferably 10—50% by weight of soap inclusive of an optionally present foam-inhibiting soap consisting of saturated fatty acids with 20—24 carbon atoms, while the proportion of (sulphonate and/or sulphate): soap lies in the range from 10:1 to 1:10, preferably in the range from 5:1 to 1:2, 110

0—80, preferably 5—40% by weight of a non-ionic surface-active compound, 115

0—6, preferably 0.5—3% by weight of a foam stabiliser, 120

0—8, preferably 0.5—5% by weight of a non-surface-active foam inhibitor, 125

while the foaming power of the surface-active component is reduced by the presence of at

least one foam inhibitor (foam-inhibiting soap and/or non-surface-active foam inhibitor).

5 Washing compositions according to the invention, which contain the above-mentioned surface-active component, may correspond, for example, to the following formulations:

(A) Heavy duty washing composition

- 10 0.5—40% by weight PPC  
5—60% by weight builder substances other than PPC,  
8—35% by weight surface-active component,  
10—40% by weight bleaching component,  
15 1—5% by weight magnesium silicate, up to 15% by weight of other usual constituents.

(B) Pre-washing composition

- 20 0.5—30% by weight PPC,  
10—70% by weight builder substances other than PPC,  
3—10% by weight surface-active component,  
25 up to 15% by weight of other usual constituents.

(C) Washing composition for fine and coloured fabrics

- 30 3—30% by weight PPC,  
10—60% by weight builder substances other than PPC,  
10—40% by weight surface-active component,  
up to 15% by weight of other usual constituents.

35 The complex-forming power for alkaline earth ions is particularly pronounced in the case of the phosphonopolycarboxylic acids, so that they are able to assist the washing process; on the other hand their complex-forming ability for heavy metals—like most other known complex-forming builder substances—is only small. It is therefore advisable to include in the builder substance component of the washing compositions such complex-forming substances in small amounts from, for example, 0.1—5, preferably 0.1—2% by weight. Ethylenediaminetetraacetic acid, di-ethylenetriaminopentaacetic acid or hydroxy-ethanediphosphonic acid or their salts are examples of suitable compounds forming complexes with heavy metals, especially copper.

50 The washing compositions of the formulations (A) to (C) contain as other conventional constituents at least one of the following components in the indicated amounts:

- 0.2 — 3% by weight dirt carrier,  
0.7 — 3% by weight enzymes,  
2 — 8% by weight textile softeners,  
0.1 — 1% by weight optical brighteners,

- 0.01—1% by weight dyestuffs and perfumes,  
0.2 — 2% by weight antimicrobial compounds,  
0 — 15% by weight water.

65 The washing compositions and washing assistants containing the phosphonopolycarboxylic acids of formula I according to the invention, in the washing of textiles of a variety of fibres of natural or synthetic origin, are marked by insensitivity towards hardness in water, even at high temperatures, and an excellent washing power. A special advantage of the builder substances to be used in the invention is their insensitivity under conditions in which sodium tripolyphosphate is already partly or wholly hydrolysed. This indifference of the phosphonopolycarboxylic acids used according to the invention is of particular importance in the process of manufacture of solid washing compositions and washing assistants most used at the present time, the hot drying of a slurry-like aqueous solution of the raw materials.

85 The solid washing compositions and washing assistants are present mostly as pourable products, which have generally a powder, granulated, agglomerated or hollow spherical form; they may however also be present in many other forms, as for example as small rods, needles or flakes.

90 By far the most useful process for the production of the powder is spray drying. In this the components present at first in pulverulent form or as aqueous solutions are mixed to a slurry or a solution. This mixture is sprayed into a drying tower through nozzles into a hot stream of air. The powder thus prepared is then in some cases mixed with other pulverulent washing agent components, which, as for example the bleaching component, are not so well suited to the spray drying. Individual washing agent constituents may also be sprayed on a powder obtained in the preparation of the washing agent, thus for example, the non-ionic detergents are often not added to the slurry, but are sprayed on a pulverulent washing agent constituent. This method is specially advisable in the case of non-surface-active foam inhibitors, which are preferably sprayed on a finished powder.

105 All other processes for the preparation of pourable washing agents may be used, so long as these guarantee the composition of the washing agent according to the invention.

115 Now follows an enumeration of the constituents present or possibly present in the washing compositions and washing assistants according to the invention arranged according to product groups.

120 The surface-active compounds of the washing compositions and washing assistants according to the invention contain in the molecule

at least one hydrophobic organic residue and water-solubilising anionic or non-ionic group. The hydrophobic residue is generally an aliphatic hydrocarbon residue having 8 to 26, preferably 10 to 22 and especially 12 to 18 carbon atoms or an alkyl-aromatic residue having 6 to 18, preferably 8 to 16 aliphatic carbon atoms.

Suitable surface-active compounds of the soap type are derived from natural or synthetic, preferably saturated fatty acids, possibly also from resin or naphthalene acids.

Suitable surface-active compounds of the sulphonate type are alkylbenzenesulphonates ( $C_6-C_{18}$ -alkyl), mixtures of alkene- and hydroxyalkane-sulphonates and also disulphonates, such as are obtained, for example, from mono-olefines with terminal or non-terminal double bonds by sulphonation with gaseous sulphur trioxide and subsequent alkaline or acid hydrolysis of the sulphonation products. Further, alkane-sulphonates are suitable which are obtainable from alkanes by sulphochlorination or sulfoxidation and subsequent hydrolysis and neutralisation or by bisulphite addition to olefines. Further useful surface-active compounds of the sulphonate type are the esters of  $\alpha$  - sulpho - fatty acids, for example the  $\alpha$  - sulphonic acids from hydrogenated methyl or ethyl esters of coconut, palm kernel or tallow fatty acids.

Suitable surface-active compounds of the sulphate type are the sulphuric acid monoesters of primary alcohols (for example from coconut fatty alcohols, tallow fatty alcohols or oleyl alcohol) and of the secondary alcohols thereof. Further, sulphated fatty acid alkanolamides, fatty acid monoglycerides or reaction products of 1 to 4 mol of ethylene oxide with primary or secondary fatty alcohols or alkylphenols are suitable.

Suitable surface-active compounds of the type of synthetic carboxylates are especially fatty acid esters or amides of hydroxy- or amino - carboxylic acids or sulphonic acids, as for example, the fatty acid sarcosides, glycollates, lactates, taurides or isethionates.

The anionic surface-active compounds may be present in the form of their sodium, potassium and ammonium salts as well as soluble salts of organic bases, such as mono-, di- or tri-ethanolamine.

Suitable non-ionic surface-active compounds of the polyglycol ether type are the products of addition of 4 to 40, preferably 4 to 20 mol of ethylene oxide to 1 mol of fatty alcohol, alkylphenol, fatty acid, fatty amine, fatty acid amide or alkanesulphonamide. The products of addition of 5 to 16 mol of ethylene oxide to coconut or tallow fatty alcohols, oleyl alcohol or secondary alcohols having 8 to 18, preferably 12 to 18 carbon atoms, as well as to mono- or di-alkylphenols having 6 to 14 carbon atoms in the alkyl residues are particularly important. Besides these

water-soluble nonionics, however, water-insoluble or not completely water-soluble polyglycol ethers having 1 to 4 ethyleneglycol-ether residues in the molecule are also of interest, especially when they are used together with water-soluble non-ionic or anionic surface-active compounds.

Furthermore, useful non-ionic surface-active compounds are the water-soluble products of addition, containing 20 to 250 ethyleneglycol-ether groups and 10 to 100 propyleneglycol-ether groups, of ethylene oxide to polypropyleneglycol (=Pluronic (registered trade mark)), alkylenediaminepolypropyleneglycol (=Tetronics (registered trade mark)) and alkylpolypropyleneglycols having 1 to 10 carbon atoms in the alkyl chain, in which the polypropyleneglycol chain functions as a hydrophobic residue.

The foaming power of the surface-active compounds can be increased or reduced by combinations of suitable types of surface-active compounds; a reduction can also be obtained by additions of non-surface-active organic substances.

Surface-active compounds of the sulphonate or sulphate type, surface-active carboxy- or sulpho-betaines, as well as the above-mentioned nonionics of the alkylolamide type are particularly suitable as foam stabilisers. Moreover, fatty alcohols or higher terminal diols have been proposed for this purpose.

A reduced foaming power, which is desired when working in machines, is frequently obtained by a combination of different types of surface-active compounds, for example, sulphates and/or sulphonates with nonionics and/or with soaps. When soaps are used the foam inhibition increases with the degree of saturation and the carbon number of the fatty acid residue; soaps of the saturated  $C_{20-24}$  fatty acids are therefore specially suitable as foam inhibitors.

The non-surface-active foam inhibitors include N - alkylated aminotriazines possibly containing chlorine, which are obtained by reaction of 1 mol of cyanuric chloride with 2 to 3 mol of a mono- and/or di-alkylamine having 6 to 20, preferably 8 to 18 carbon-atoms in the alkyl residue. Propoxylated and/or butoxylated aminotriazines have a similar action, for example products which are obtained by addition of 5 to 10 mol of propylene oxide on to 1 mol of melamine and further addition of 10 to 50 mol of butylene oxide to this propylene oxide derivative.

Water-insoluble organic compounds such as paraffins or halo - paraffins with melting points below  $100^\circ\text{C}$ , aliphatic  $C_{18}$  to  $C_{40}$  ketones, as well as aliphatic carboxylic acid esters, which contain in the acid or alcohol residue, possibly in both of these residues, at least 18 carbon atoms (for example triglycerides or fatty acid fatty alcohol esters) are also suitable as non-surface-active foam inhibitors;

70

75

80

85

90

95

100

105

110

115

120

125

130

they can be used above all in combinations of surface-active compounds of the sulphate and/or sulphonate type with soaps for the inhibition of the foam.

- 5 Specially low-foaming nonionics, which may be used both alone and in combination with the said anionic and the other non-ionic surface-active compounds and reduce the foaming power of strongly foaming surface-active compounds, are the products of addition of propylene oxide to the already mentioned surface-active polyethyleneglycolethers as well as the likewise already described products of addition of ethylene oxide to polypropyleneglycols and to alkylenediamino - polypropyleneglycols or to  $C_{1-10}$  alkylpolypropyleneglycols.

- Further builder substances in combination with the phosphonopolycarboxylic acids which are suitable are weakly acid, neutral or alkaline reacting inorganic or organic salts, especially alkali metal salts, which precipitate calcium ions or are able to form complexes therewith.

- 25 Suitable inorganic salts are especially the alkali metal carbonates and bicarbonates as well as the alkali metal silicates, for example sodium silicates with a ratio of  $Na_2O$  to  $SiO_2$  of 1:1 to 1:3.5. The sulphates and borates of the alkali metals are also useful.

- The suitable organic salts include the non-surface-active sulphonic acids, carboxylic acids and sulphocarboxylic acids containing 1 to 35 8 carbon atoms, for example alkali metal salts of benzene -, toluene - or xylene - sulphonic acids, sulphobenzoic acid, sulphophthalic acid, sulphoacetic acid, sulphosuccinic acid or other sulphocarboxylic acids, and also the salts of acetic acid or lactic acid.

- Further suitable organic builder substances are the nitrogen- and phosphorus-free compounds forming complexes with calcium ions of the type of polycarboxylic acids or their salts, among which are also polymerisates containing carboxylic groups. For example, citric acid, tartaric acid, benzenhexacarboxylic acid, polycarboxylic acids containing carboxymethyl-ether groups, such as for example diglycollic acid, 2,2' - hydroxydisuccinic acid, and polyhydric alcohols or hydroxycarboxylic acids partly or completely etherified with glycollic acid, for example bis(O - carboxymethyl) - ethyleneglycol, mono - or bis - (O - carboxymethyl) - glyceric acid or carboxymethylated or oxidised polysaccharides. The polymeric carboxylic acids with a molecular weight of at least 350 of the type of polyacrylic acid, poly -  $\alpha$  - hydroxyacrylic acid, polymaleic acid and so on, as well as the salts of copolymers of maleic anhydride with ethylene, propylene or vinylmethylether and the polyhydroxycarboxylic acids obtained by copolymerisation of acrolein and acrylic acid in the presence of hydrogen peroxide and subse-

quent reaction according to the Cannizzar reaction are also suitable.

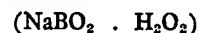
In particular, the builder substances are selected from the constituents of the washing compositions and washing assistants according to the invention so that the preparations have a weak acid or weak alkaline reaction; i.e. the pH value of a 1% solution of the preparations should lie in the range from 6 to 11.5. The fine and coloured washing compositions thereby give a very weak acid to weak alkaline reaction (pH value = 6 to 9.5), while soaking, prewashing and boiling washing compositions are adjusted to be rather more strongly alkaline (pH value = 9.5 to 11.5, preferably 10 to 11).

In the preparations according to the invention dirt carriers may also be contained, which hold suspended in the bath the dirt detached from the fibres and thus prevent the greying. For this purpose water-soluble colloids mostly of organic nature are suitable, as for example glue, gelatine, salts of ethercarboxylic acids or ethersulphonic acids of starch or cellulose or salts of acid sulphuric acid esters of cellulose or starch. In addition water-soluble polyamides containing acid groups are suitable for this purpose. Further, soluble starch preparations and other starch products than those mentioned above can be used, as for example, degraded starch, aldehyde starches and so on. Polyvinylpyrrolidone is also useful. The products of addition of 1 to 4 mol of ethylene oxide to 1 mol of fatty alcohol having 8 to 18 carbon atoms already described as non-ionic surface-active compounds, also possess dirt-carrying properties.

Among the compounds serving as bleaching agents which provide  $H_2O_2$  in water, sodium perborate tetrahydrate



and the monohydrate



have special importance as the bleaching component. However, other borates yielding  $H_2O_2$  are also useful, for example perborax



These compounds may be partly or wholly replaced by other active oxygen carriers, especially by peroxyhydrates, such as peroxy-carbonates



peroxyphosphates, citrate perhydrates, urea -  $H_2O_2$  - or melamine -  $H_2O_2$  - compounds as well as salts of peracids yielding  $H_2O_2$ , as for example salts of Caro's acid ( $KHSO_5$ ), perbenzoates or peroxyphthalates.

It is advisable to incorporate 0.25 to 10%

by weight of the usual water-soluble and/or water-insoluble stabilisers for the peroxy-compounds together with the latter. Suitable water-insoluble stabilisers, which for example constitute 1 to 8, preferably 2 to 7% of the weight of the total preparation, are the magnesium silicates mostly obtained by precipitation from aqueous solutions,  $\text{MgO}:\text{SiO}_2 = 4:1$  to  $1:4$ , preferably  $2:1$  to  $1:2$  and especially  $1:1$ . Other alkaline earth metal, cadmium or tin silicates of corresponding composition are utilisable in their place. Water-containing tin oxides are also suitable as stabilisers. Water soluble stabilisers, which may be present together with water-insoluble stabilisers, are the organic complex-forming compounds, which may constitute 0.25 to 5, preferably 0.5 to 2.5% of the weight of the total preparation.

In order to attain a satisfactory bleaching action during the washing even at temperatures below  $80^\circ\text{C}$ , especially in the range from  $60^\circ$  to  $40^\circ\text{C}$ , activator-containing bleaching components are preferably incorporated in the preparations.

As activators for per-compounds yielding  $\text{H}_2\text{O}_2$  in water are specified N - acyl - and O - acyl compounds forming organic peracids with this  $\text{H}_2\text{O}_2$ , as well as carbonic acid or pyrocarbonic acid esters, the activation value for the per-compounds (=titre) of which is at least 3, preferably at least 4.5. This activation value is estimated in the following way:

Solutions, which contain 0.615 g/litre of  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  (4 mMol/litre) and 2.5 g/litre of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$

after heating to  $60^\circ\text{C}$  are treated with 4 mMol/litre of activator and maintained for 5 minutes with stirring at the indicated temperature. Then 100 ml of this liquid is added to a mixture of 250 g of ice and 15 ml of glacial acetic acid and immediately after addition of 0.35 of potassium iodide, the product is titrated with 0.1 N sodium thiosulphate solution and starch as indicator. The amount of thiosulphate solution thereby consumed in ml is the activation value (=titre); with a 100% activation of the peroxide used, it was 8.0 ml.

The activators utilisable according to the invention include especially the N - diacylated and N,N' - tetraacylated amines, as for example, N,N,N',N' - tetraacetyl - methylenediamine or - ethylenediamine, N,N - diacetylaniline and N,N - diacetyl - p - toluidine and 1,3 - diacylated hydantoin, as for example the compounds 1,3 - diacetyl - 5,5-dimethylhydantoin and 1,3 - dipropionyl - hydantoin, as well as the compounds tetraacetylglucuril and tetrapropionylglucuril.

In the activation of the per-compounds by the said N - acyl - and O - acyl compounds, carboxylic acids, as for example, acetic acid, propionic acid, benzoic acid, become free; it is usually advisable to add basic salts to bind these carboxylic acids. In the case of effective activators an activation even with added amounts of 0.05 mol of activator per gram-atom of active oxygen can be observed. It is preferred to work with 0.1 to 1 mol of activator; the amount may of course also be increased to 2 mol of activator per gram-atom of active oxygen.

The washing compositions may contain as optical brighteners for cotton, especially derivatives of diaminostilbenedisulphonic acid or its alkali metal salts. For example, salts of 4,4' - bis(2 - anilino - 4 - morpholino - 1,3,5 - triazine - 6 - yl - amino) - stilbene - 2,2' - disulphonic acid or similarly constructed compounds which instead of the morpholino group carry a diethanolamino-group, a methylamino group or a 2 - methoxyethylamino group are suitable. Suitable brighteners for polyamide fibres may be of the type of 1,3 - diaryl - 2 - pyrazolines, for example the compound 1 - (p - sulphamoylphenyl) - 3 - (p - chlorophenyl) - 2 - pyrazoline as well as similarly constructed compounds, which instead of the sulphamoyl group carry, for example, the methoxycarbonyl, 2 - methoxyethoxycarbonyl, acetylamino or vinylsulphonyl group. Further, useful polyamide brighteners are the substituted aminocoumarines, for example 4 - methyl - 7 - dimethylamino - or 4 - methyl - 7 - diethylamino - coumarin. In addition, the compounds 1 - (2 - benzimidazolyl) - 2 - (1 - hydroxyethyl - 2 - benzimidazolyl) - ethylene and 1 - ethyl - 3 - phenyl - 7 - diethylamino - carbostyryl are useful as polyamide brighteners. The compounds 2,5 - di(2 - benzoxazolyl) - thiophene, 2 - (2 - benzoxazolyl) - naphtho[2,3 - b] - thiophene and 1,2 - di - (5 - methyl - 2 - benzoxazolyl) - ethylene are suitable as brighteners for polyester and polyamide fibres. Further, brighteners of the type of the substituted 4,4' - distyryldiphenyl may be present; for example the compound 4,4' - bis(4 - chloro - 3 - sulphostyryl) - diphenyl. Mixtures of the above-mentioned brighteners may also be used.

The enzyme preparations to be used are mostly a mixture of enzymes with different action, for example a mixture of proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. Enzymes obtained from the strains of bacteria or fungi such as *Bacillus subtilis* or *Streptomyces griseus* are of special interest, especially proteases or amylases, which are relatively stable towards alkali, percompounds and anionic surface-active compounds and are still effective at temperatures up to  $70^\circ\text{C}$ .

Enzyme preparations are marketed by the manufacturers mostly as aqueous solutions of the active substances or as powders, granulates or as cold sprayed products. They frequently contain as diluents or extenders sodium sulphate, sodium chloride, alkali metal ortho-, pyro- or poly-phosphates, especially tripolyphosphate. Dust-free preparations are of particular value; they are obtained in known way by incorporation of oily or paste-like nonionics or by granulation by the aid of melts of salts containing water of crystallisation, in their own water of crystallisation.

Enzymes may be incorporated which are specific for a particular type of dirt, for example proteases or amylases or lipases. Combinations of enzymes of different action especially combinations of proteases and amylases, are preferably used.

#### Examples

The following examples describe compositions of a few preparations according to the invention. The phosphonopolycarboxylic acids as well as the salt-like surface-active compounds and the other organic and inorganic salts are present as the sodium salts. The following symbols or abbreviations are used.

"ABS": the salt of an alkylbenzenesulphonic acid essentially with 11 to 13 carbon atoms in the alkyl chain; obtained by condensation of straight-chain olefines with benzene and sulphonation of the alkylbenzene thus obtained;

"Fs-estersulphonate": the salt of a sulphonic acid obtained from the methyl ester of a hardened tallow fatty acid by sulphonation with  $\text{SO}_3$ ;

"Alkanesulphonate": the salt of a sulphonic acid obtained from paraffins having 12 to 16 carbon atoms using the method via the sulfoxidation;

"KA-sulphate" and "TA-sulphate": the salts of sulphated, substantially saturated fatty alcohols prepared by reduction of coconut fatty acid and tallow fatty acid respectively;

"OA+10 EO": a product of addition of ethylene oxide (EO) to technical oleyl alcohol (OA) in the molar ratio 10:1;

"Perborate": a product containing about 10% of active oxygen of the approximate composition



"EDTA" and "HEDP": the salts of ethylenediaminetetraacetic acid and hydroxyethanediphosphonic acid respectively;

"CMC": the salt of carboxymethylcellulose.

The soap used was prepared from a fatty acid mixture of iodine value 3 and the following composition: 9% by weight  $\text{C}_{18}$ , 14% by weight  $\text{C}_{20}$  and 77% by weight  $\text{C}_{22}$ .

A mixture of about 45% of a  $\text{N}_2\text{N}'$  - di-(alkylamino) - chlorotriazine and about 55% of a  $\text{N}_2\text{N}'\text{N}''$  - tri - (alkylamino) - triazine was used in the examples as the non-surface-active foam inhibitor. In these triazine derivatives the alkyl residues are present as a mixture of homologues having 8 to 18 carbon atoms. The monochlorotriazine derivative or the trialkylaminotriazine can also be used with a similar result. In the production of the preparations the non-surface-active foam inhibitor was sprayed on the pulverulent preparation.

#### Example 1

Heavy duty washing composition  
 24.0% by weight 1 - phosphonobutane - 2,3,4 - tricarboxylic acid  
 5.5% by weight ABS  
 2.2% by weight TA-sulphate  
 1.5% by weight KA-sulphate  
 0.2% by weight EDTA  
 6.0% by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
 27.0% by weight perborate  
 2.0% by weight  $\text{MgSiO}_3$   
 0.3% by weight cotton brightener  
 1.5% by weight CMC  
 0.6% by weight non-surface-active foam inhibitor  
 Remainder sodium sulphate and water.

#### Example 2

Heavy duty washing composition  
 5.0% by weight 2 - phosphonobutane - 1,2,4 - tricarboxylic acid  
 2.5% by weight OA+10 EO  
 6.0% by weight Fs-estersulphonate  
 2.0% by weight soap  
 0.3% by weight HEDP  
 15.0% by weight  $\text{Na}_2\text{CO}_3$   
 5.0% by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
 15.0% by weight perborate  
 1.0% by weight  $\text{MgSiO}_3$   
 5.0% by weight tetraacetylglycuril  
 10.5% by weight cotton brightener  
 1.2% by weight CMC  
 0.4% by weight non-surface-active foam inhibitor  
 Remainder sodium sulphate and water.

#### Example 3

Heavy duty washing composition  
 15.0% by weight 2 - phosphonopropane-2,3 - dicarboxylic acid  
 8.5% by weight Fs-estersulphonate  
 4.0% by weight TA-sulphate  
 2.0% by weight soap  
 5.5% by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
 26.0% by weight perborate  
 1.0% by weight  $\text{MgSiO}_3$   
 0.6% by weight cotton brightener  
 1.6% by weight CMC  
 0.2% by weight non-surface-active foam inhibitor  
 Remainder sodium sulphate and water.



## Example 4

## Heavy duty washing composition

- 15.0% by weight 1 - phosphonoethane -  
1,2 - dicarboxylic acid  
5 10.0% by weight alkanesulphonate  
2.5% by weight OA+10 EO  
3.5% by weight soap  
1.2% by weight EDTA  
8.0% by weight  $\text{Na}_2\text{CO}_3$   
10 8.0% by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
26.5% by weight perborate  
1.0% by weight  $\text{MgSiO}_3$   
0.3% by weight cotton brightener  
0.8% by weight CMC  
15 0.2% by weight non-surface-active foam  
inhibitor  
Remainder sodium sulphate and water.

## Example 5

## Heavy duty washing composition

- 20 0.75% by weight 2 - phosphonobutane-  
1,2,4 - tricarboxylic acid  
18.0 % by weight Fe-estersulphonate  
4.0 % by weight ABS  
2.5 % by weight OA+10 EO  
25 3.5 % by weight EDTA  
10.0 % by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
20.0 % by weight  $\text{Na}_2\text{CO}_3$   
30.0 % by weight perborate  
1.5 % by weight  $\text{MgSiO}_3$   
30 1.2 % by weight CMC  
0.5 % by weight non-surface-active foam  
inhibitor  
0.4 % by weight cotton brightener  
Remainder sodium sulphate and water.

## Example 6

## Prewashing composition

- 35 3.0% by weight 1 - phosphonopropane-  
1,2,3 - tricarboxylic acid  
5.0% by weight OA+10 EO  
40 10.0% by weight  $\text{Na}_2\text{O}$ , 3.3 $\text{SiO}_2$   
15.0% by weight  $\text{Na}_2\text{CO}_3$   
1.0% by weight CMC  
2.3% by weight enzymes  
Remainder sodium sulphate and water.

## Example 7

## Light duty washing composition

- 45 10.0% by weight 2 - phosphonobutane-  
2,3,4 - tricarboxylic acid  
1.5% by weight KA-sulphate  
50 1.5% by weight TA-sulphate  
8.0% by weight Fs-estersulphonate  
3.0% by weight OA+10 EO  
3.0% by weight soap  
1.5% by weight CMC  
55 5.0% by weight  $\text{NaHCO}_3$   
8.0% by weight  $\text{Na}_2\text{CO}_3$   
0.3% by weight cotton brightener  
0.2% by weight polyamide brightener  
Remainder sodium sulphate and water.

- 60 The preparations according to Examples 1

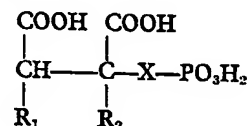
to 7 have in 1% aqueous solutions a pH value which lies below 11.5.

The washing compositions and washing assistants according to the invention have a substantially smaller phosphorus content than corresponding preparations based on tripolyphosphate. Above all, on washing in hard water incrustations on the washing and formation of fur on washing machine parts can be avoided by use of the preparations according to the invention.

## WHAT WE CLAIM IS:—

1. A washing composition or washing assistant, which contains:

(I) 0.5 to 70% by weight of a phosphonopolycarboxylic acid of formula I

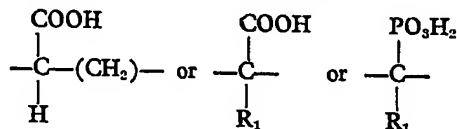


(I)

or water-soluble salt thereof, in which  $\text{R}_1$  represents a hydrogen atom or a methyl residue,  $\text{R}_2$  represents a hydrogen atom, an alkyl residue having 1 to 4 carbon atoms or the residue



wherein  $\text{R}_1$  is as defined above and X represents a direct bond or the group



wherein  $\text{R}_1$  is as defined above and in which preferably a maximum of three carboxyl groups may be present,

(II) 0 to 96.5% by weight of a complex-forming and/or non-complex-forming builder substance, other than (I), above,

(III) 3 to 45% by weight of at least one surface-active compound from the group of soaps, synthetic carboxylates, sulphates, sulphonates and non-ionic polyglycol ethers, and the constituents of the washing composition or washing assistants is chosen so that the preparations have a pH value between 6 and 11.5 in 1% aqueous solution.

2. A composition as claimed in claim 1 in which the builder substances of component II are phosphorus-free.

3. A composition as claimed in claim 1 in which the pH value is between 7 and 11.

4. A composition as claimed in any one of claims 1 to 3 in which the pH value results from the choice of phosphonopolycarboxylic acid or a salt thereof of component (I) and



- other builder substances of component (II).
5. A composition as claimed in claim 1 or claim 3 in which the total phosphorus content is not over 4% by weight.
- 5 6. A composition as claimed in claim 5 in which the total phosphorus content is not over 2% by weight.
7. A composition as claimed in claim 1, 3, 5 or 6 which contains a phosphonopolycarboxylic acid of formula I or a water soluble salt thereof and an alkali metal carbonate and/or an alkali metal silicate, and the proportion by weight of phosphonopolycarboxylic acid or salt thereof to the carbonate and/or silicate
- 10 lies between 1:100 and 4:1.
8. A composition as claimed in claim 7 in which the proportion is between 1:50 and 4:1.
9. A composition as claimed in claim 7 in which the proportion is between 1:20 to 1:1.
- 20 10. A foam-inhibited washing composition suitable for use in washing machines and as claimed in any one of claims 1 to 9 in which the surface-active component (III) has the following composition:
- 25 (a) 8 to 95% by weight of one or more surface-active compounds of the sulphonate and/or sulphate type,
- (b) 0 to 80% by weight of soap and the proportion of (sulphonate and/or sulphate): soap lies in the range from 10:1 to 1:10.
- 30 (c) 0 to 80% by weight of a non-ionic surface-active compound,
- (d) 0 to 6% by weight of a foam stabiliser,
- 35 (e) 0 to 8% by weight of a non-surface-active foam inhibitor,
- and the foaming power of the surface-active component is reduced by the presence of at least one foam inhibitor (foam inhibiting soap and/or non-surface-active foam inhibitor).
- 40 11. A composition as claimed in claim 10 containing 25 to 75% by weight of component (a), 10 to 50% by weight of component (b), 5 to 40% by weight of component (c), 0.5 to 3% by weight of component (d) and 0.5 to 5% by weight of component (e).
- 45 12. A composition as claimed in claim 10 or 11 in which the soap of component (b) includes a fraction of foam inhibiting soap consisting of saturated fatty acids having 20 to 24 carbon atoms.
- 50 13. A composition as claimed in claim 10, 11 or 12 in which the proportion of (sulphonate and/or sulphate) soap lies in the range of 5:1 to 1:2.
- 55 14. A washing composition as claimed in any one of the preceding claims which contains a bleaching component comprising a peroxy-compound and a stabiliser for the peroxy compound, the bleaching component amounting to 10 to 50% by weight of the total washing composition.
- 60 15. A washing composition as claimed in claim 14 in which the bleaching component amounts to 15 to 40% by weight.
- 65 16. A washing composition or washing assistant as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.
- 70

W. P. THOMPSON & CO.,  
Coopers Buildings,  
12, Church Street,  
Liverpool, L1 3AB.  
Chartered Patent Agents.